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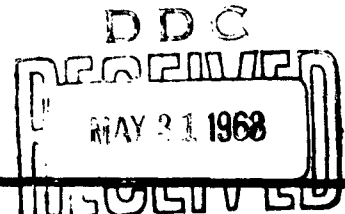
Iron-Chromium-Nitrogen Alloys

by

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ABSTRACT.

This report is a continuation of the Second Annual Technical Report, 28th February 1962. The aim of the work is to determine the solubility of CrN in ferrite by means of internal friction. The internal friction was measured with a torsional pendulum oscillating at 1 c.p.s., the amplitude being measured with a lamp at scale 3m distant.

The material was an alloy of iron and 0.94%Cr made by melting and casting in vacuum high purity iron (British Iron and Steel Research Association Grade A.H.) and high purity chromium. The ingot was processed to 0.027 in.dia. wire. Nitrogen was introduced into the specimens by heating in partly cracked ammonia, the amount of nitrogen being controlled by the degree of cracking of the ammonia.

The nitrogen content and a d.c. magnetic field saturating the specimen longitudinally both affect the amplitude dependence of the internal friction. Both effects are believed to originate in magnetic domain wall movement.

Solubility measurements were confined to the temperatures 700, 750 and 800°C at higher temperatures austenite formed and at lower temperatures the nitrogen concentration in solution was too low to measure accurately. Within this temperature range the solubility could be represented by

$$\log [\text{Cr}] [\text{N}] = 5.0 - 7650/T.$$

Iron-Chromium Nitrogen Alloys.

Although this research has as its primary object the determination of the solubility of chromium nitride in alpha iron some interesting results due to magneto-elastic damping have been found. It is necessary to examine these before dealing with the solubility results.

All the experiments were carried out on a 0.94%Cr iron alloy melted and cast in vacuum and made from elements of high purity. The ingot was hot rolled to 0.25 in. dia. then all the internal friction tests were carried out by oscillating in torsion a 0.027 in. dia. wire, the amplitude being measured on a lamp and scale, 3m. distant.

Magneto-elastic Damping.

Until recently it was thought that at low frequencies, the only damping of a ferromagnetic material arising from its ferromagnetism was (apart from eddy current losses) magneto-elastic static hysteresis (1). Since this is frequency independent but amplitude dependent most workers, including the writers, have thought it sufficient to show that the internal friction of a sample was amplitude independent in order to be able to claim that magneto-elastic effects were absent. Amplitude independence is generally found if sufficiently small amplitudes are used.

Recent work by Maringer (2)(3) and Fischbach (4) shows that in certain cases ferromagnetism may cause a maximum in the internal friction-temperature curve and that the peak occurs even at extremely small amplitudes of vibration. Maringer found an internal friction peak in iron carbon alloys and in iron nitrogen alloys at a few degrees of temperature above the Snoek peak, while Fischbach working with iron aluminium alloys found a peak on the high temperature side of the Zener peak. It seems possible that whenever a peak of anelastic origin occurs a magneto-elastic peak also occurs but at a slightly higher temperature.

In the present work on iron chromium nitrogen alloys two peaks are found corresponding to the two Snoek peaks.

Fig.1 shows the results for a specimen without a magnetic field and Fig.2 results when a longitudinal magnetic field of about 230 oe. was applied. In both cases, the two main peaks at 25°C and at 55°C respectively (for method see Report No.2) has been subtracted from the experimental. As before, for the first peak the value of $\Delta H = 18,600 \text{ cal/g.atom}$ due to Fast & Verrijp (5) has been used for the first peak and our own value of 14,000 cal/g.atom for the second peak.

Apart from a small rise on the high temperature end, it can be seen from Fig.2 that the internal friction is entirely due to these two peaks when a magnetic field is used. However when no magnetic field is used an extra peak at about 40°C appears together with a much larger rise with temperature above about 65°C. There may be a small peak hidden in this rise but one cannot be certain of this.

Since the peak at 40°C does not occur in the absence of nitrogen it is probably due to the movement of magnetic domain walls hindered by nitrogen atoms. This general idea is confirmed by a study of the amplitude dependence of the internal friction.

The internal friction of a specimen containing very little nitrogen (no Snoek peaks were observed) was found to be strongly amplitude dependent at all temperatures - see Fig.3. On the other hand a specimen with only 0.001% more nitrogen in had an internal friction which was practically independent of strain amplitude over the range tested - see Fig.4. The specimen used for Fig.3 gives similar amplitude independence when tested with a magnetic field.

The amplitude of vibration is given in cm. on a scale 3m. from the specimen, 1cm. deflection is equivalent to a surface shear strain in the specimen of 1.125×10^{-5} .

The effect of varying the current through the coil surrounding the specimen is shown in Fig.5, where it can be seen that the internal friction is becoming independent of the current at about 1 amp. (equivalent to about 226 oersteds). It was not possible to use higher currents due to heating of the coil.

Solubility Results.

As shown in a previous report (6) the solubility of the nitride in ferrite can be calculated only if both the nitrogen and chromium concentration in solution in ferrite is known. The nitrogen content can be deduced from internal friction results, while the chromium in solution can be calculated if, in addition the total nitrogen content is known. This was obtained by chemical analysis.

The results for samples nitrided at 700°C are given in Table I. This replaces the table on p.19 (Ref.6) as the calculation has now been made more accurate by allowing for a small amount of background internal friction.

TABLE I.

Specimen	Total Nitrogen % Chem. Analysis	Nitrogen in Solution % I.F.	Cr in Solution % Calculated	10^3 [Cr] [N]
B29	0.099	0.00674	0.597	4.03
B30	0.150	0.00467	0.40	1.87
B32	0.192	0.01252	0.27	3.38
B33	0.150	0.00756	0.41	3.10
B23*	0.0385	0.00517	0.82	4.24

* Not analysed but nitrogen content assumed from previous results and method of preparation.

The method of calculating the chromium in solution is now given for B29 as an example (Table I). The nitrogen precipitated is the total less that remaining in solution i.e. $0.099 - 0.00674 = 0.09226\%$. Since the precipitate has been shown to be CrN then the chromium precipitated is $0.09226 \times 52/14 = 0.343\%$. This from the total chromium, 0.94% gives the chromium in solution, i.e. 0.597%.

The fact that the chromium in solution is substantially different from the original means that the calculation of the nitrogen in solution from the internal friction results must be remade.

The nitrogen in solution is directly proportional to the sum of the peaks ($\sum P$) of the internal friction/temperature curve. It has been found experimentally that for the 0.94%Cr alloy

$$[N] = 2.16 \sum P.$$

This is quite different from the figure of 0.94 found for iron nitrogen alloys. It is therefore necessary to interpolate between these two values according to the chromium remaining in solution. The interpolated value of the proportionality constant, k , is given in Table 2. The nitrogen in solution calculated from $k \times \sum P$ is also given, together with the new value of $[Cr]$ $[N]$.

TABLE II.

Specimen	Cr %	k	$10^3 \frac{[N]}{\%}$	$10^3 \frac{[Cr]}{[N]}$	Time of Nitriding Hours.
B29	0.59	1.7	5.27	3.11	4
B30	0.39	1.4	3.02	1.18	30
B32	0.25	1.2	6.96	1.74	17½
B33	0.40	1.4	4.9	1.96	13
B23	0.82	2.0	4.8	3.91	2

There is a tendency for the value of $\frac{[Cr]}{[N]}$ to decrease with time indicating that for all but the longest times precipitation is not quite complete. A plot of the solubility product against time is shown in Fig.6.

Results were similarly obtained for 750°C and 800°C - see Table III.

TABLE III.

Temp. °C.	Specimen	Cr %	k	$10^3 \frac{[N]}{\%}$	$10^3 \frac{[Cr]}{[N]}$	Time of Nitriding Hours.
750	B45	0.86	2.05	5.67	4.88	16
	B46	0.85	2.05	5.22	4.43	18
800	B41	0.91	2.16	8.2	7.5	15
	B42	0.907	2.16	8.85	8.03	24
	B43	0.858	2.05	9.76	7.81	75

In the case of 800°C precipitation appears to be practically complete after 15 hrs.

-2-

The plot of $\log [\text{Cr}] [\text{N}]$ against the inverse of the absolute temperature is shown in Fig.7 together with the results of previous calculations. Only the lowest two points are used for 700°C as these correspond to the longest times of nitriding. The lines joining the points at 700°C to those at 800°C fall below the points for 750°C, but this is not surprising in view of the rather short times used for the latter temperatures.

The slopes of the lines drawn give heats of solution of 31,100 and 38,900 making an average of 35,000 cal/g.atom. This is very close to the heats of solution of both calculations. It is concluded that the solubility of CrN in ferrite is represented by the equation

$$\log [\text{Cr}] [\text{N}] = 5.0 - 7650/T$$

It is probable that greater accuracy may be obtained by using a lower chromium content and thus a higher nitrogen content in solution which could be measured more accurately. However, for most purposes the figures obtained are sufficiently accurate and in view of the fact that many commercial alloys contain much more chromium it is considered more profitable to extend the experiment to include a 10% Cr alloy. From the value of $[\text{Cr}] [\text{N}]$ found above one would expect a negligible concentration of nitrogen in solution in equilibrium with CrN in the case of a 10%Cr alloy.

Preliminary experiments however indicate that a significant amount of nitrogen remains in solution and it is proposed to measure this as soon as possible.

Conclusions. The solubility of CrN in ferrite when the %Cr is 1 or less is

$$\log [\text{Cr}] [\text{N}] = 5.0 - 7650/T$$

in the temperature range 700-800°C.

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Dr. T. B. Koshal left the Department of Metallurgy on the 1st Nov.1962 and is now with Richard Thomas & Baldwins Ltd., Llanwern, Newport, Mon.

Dr. Rawlings was away for 3 months from this work during this period.

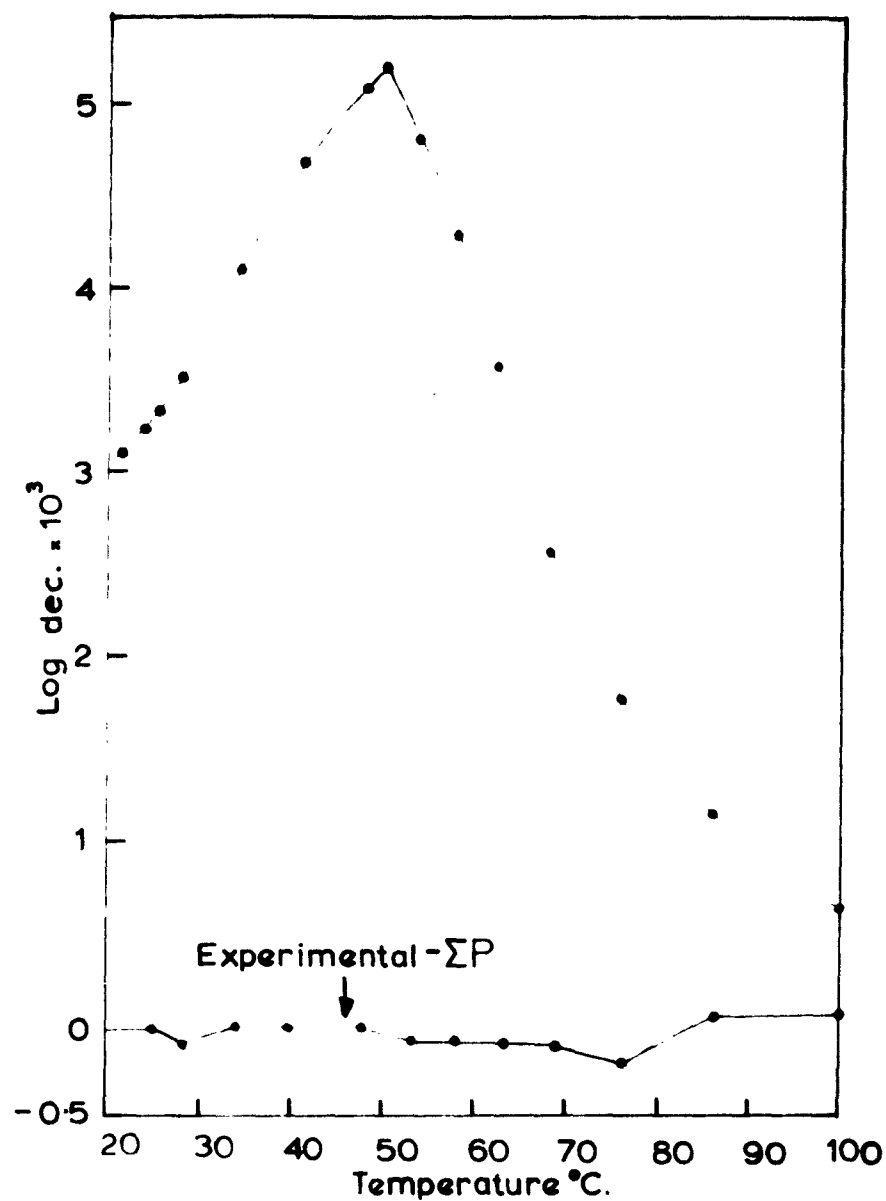
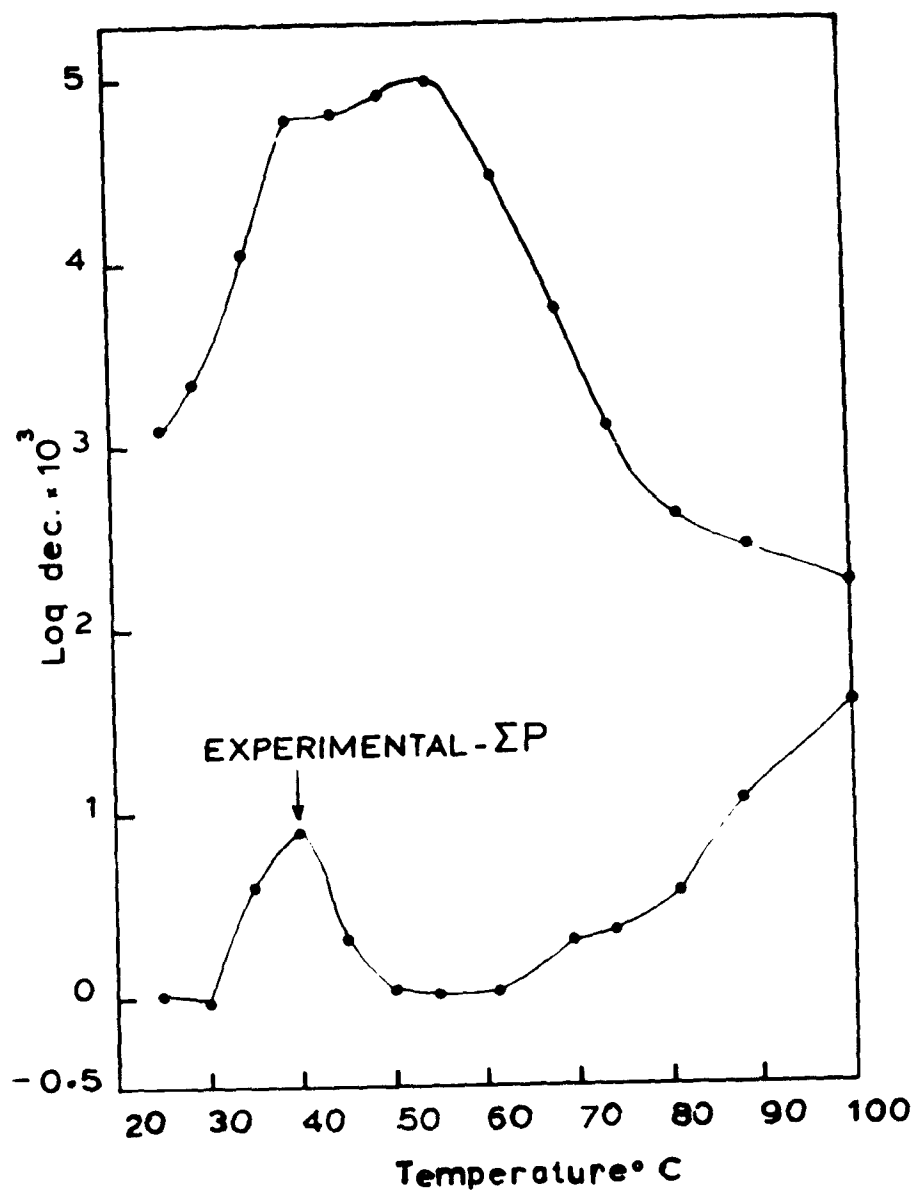


Fig. 1

INTERNAL FRICTION / TEMP. CURVE FOR SPECIMEN
NITRIDED AND QUENCHED FROM 800°C .

(0.94% Cr Alloy)

Specimen magnetised with a d.c. field of 226 oe.



INTERNAL FRICTION / TEMP. CURVE FOR SPECIMEN
NITRIDED AND QUENCHED FROM 800°C.
(0.94% Cr Alloy)

Measurement taken without a magnetic field.

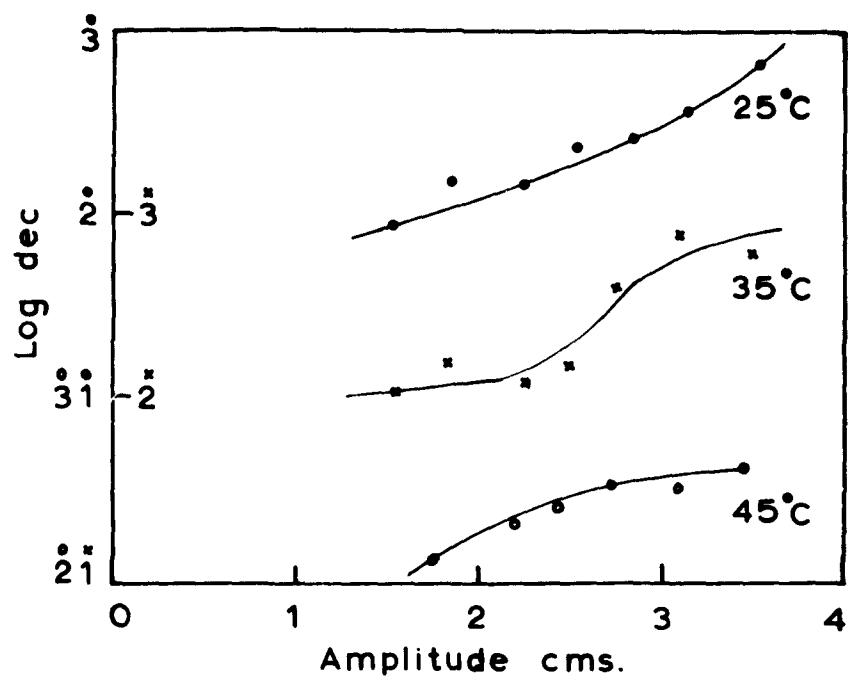


Fig.3

VARIATION OF LOG DEC WITH AMPLITUDE
AT DIFFERENT TESTING TEMPERATURES FOR
AN ANNEALED 0.94% Cr ALLOY.

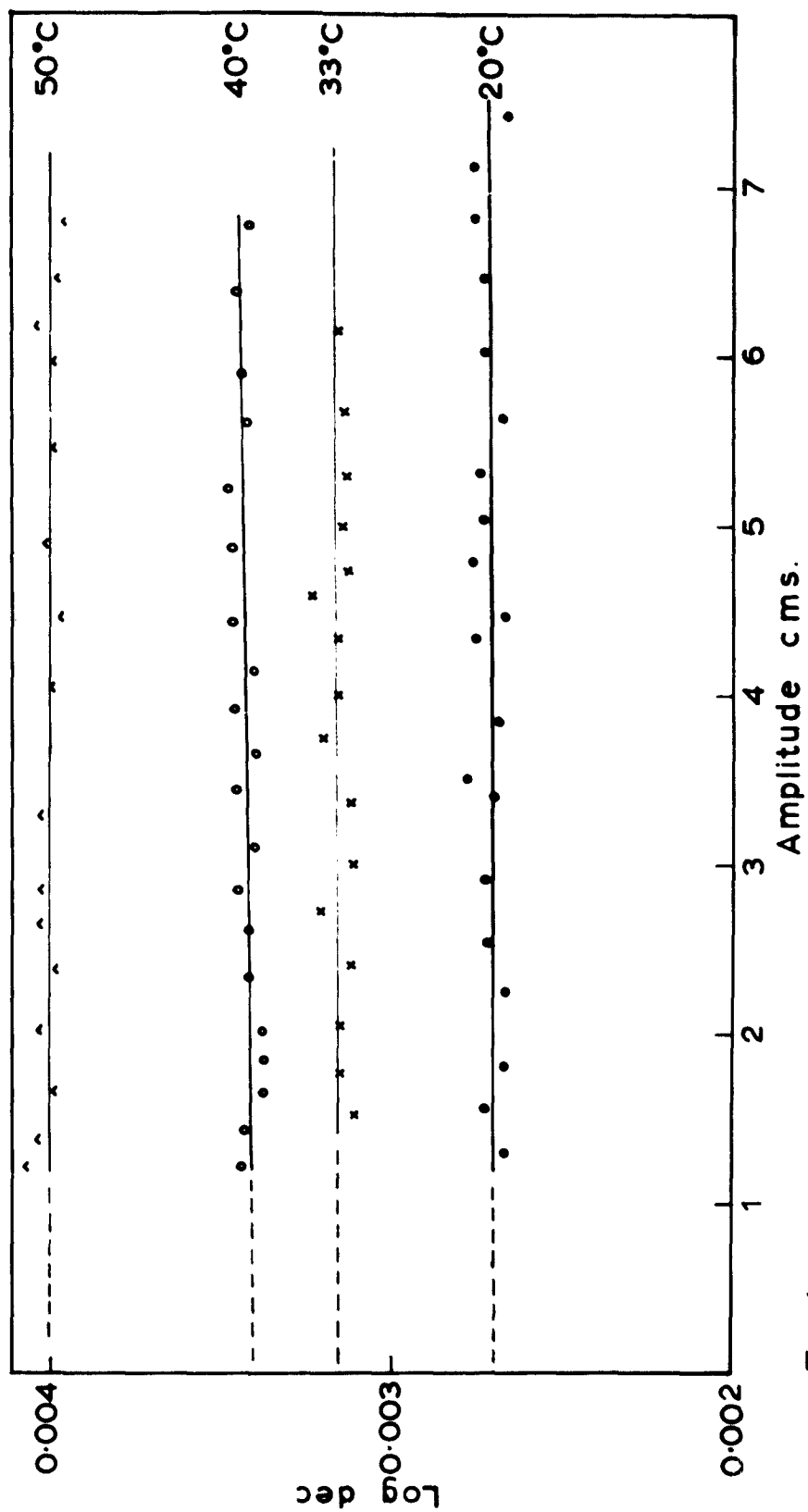


Fig.4

VARIATION OF LOG DEC WITH AMPLITUDE FOR A NITRIDED 0.94 Cr ALLOY.

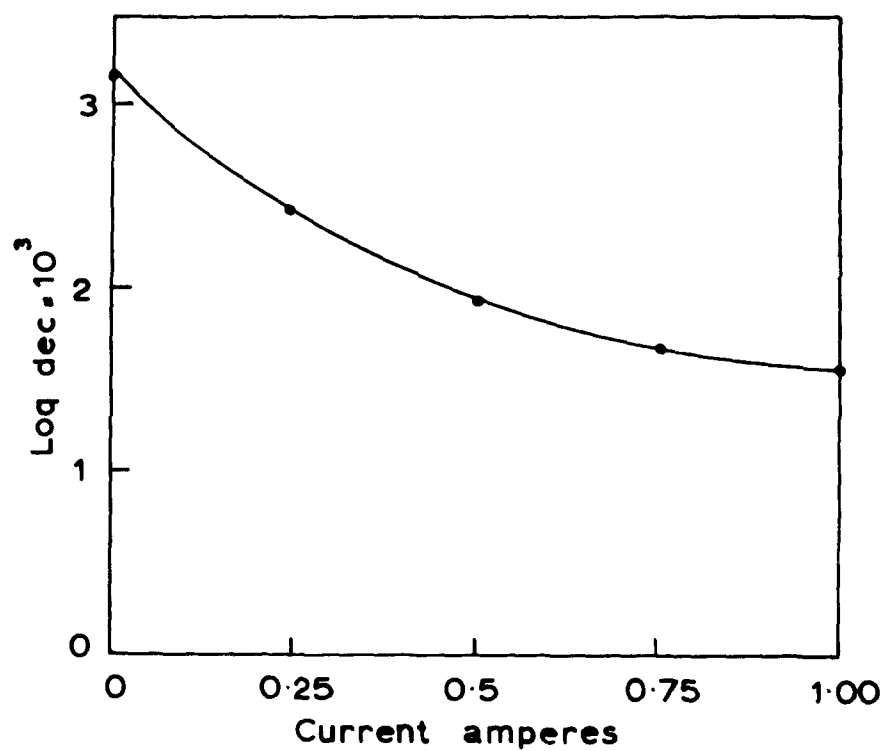


FIG. 5

THE EFFECT OF A D.C. CURRENT ON THE
ROOM TEMPERATURE LOG. DEC. OF AN
ANNEALED 0.94% Cr ALLOY.

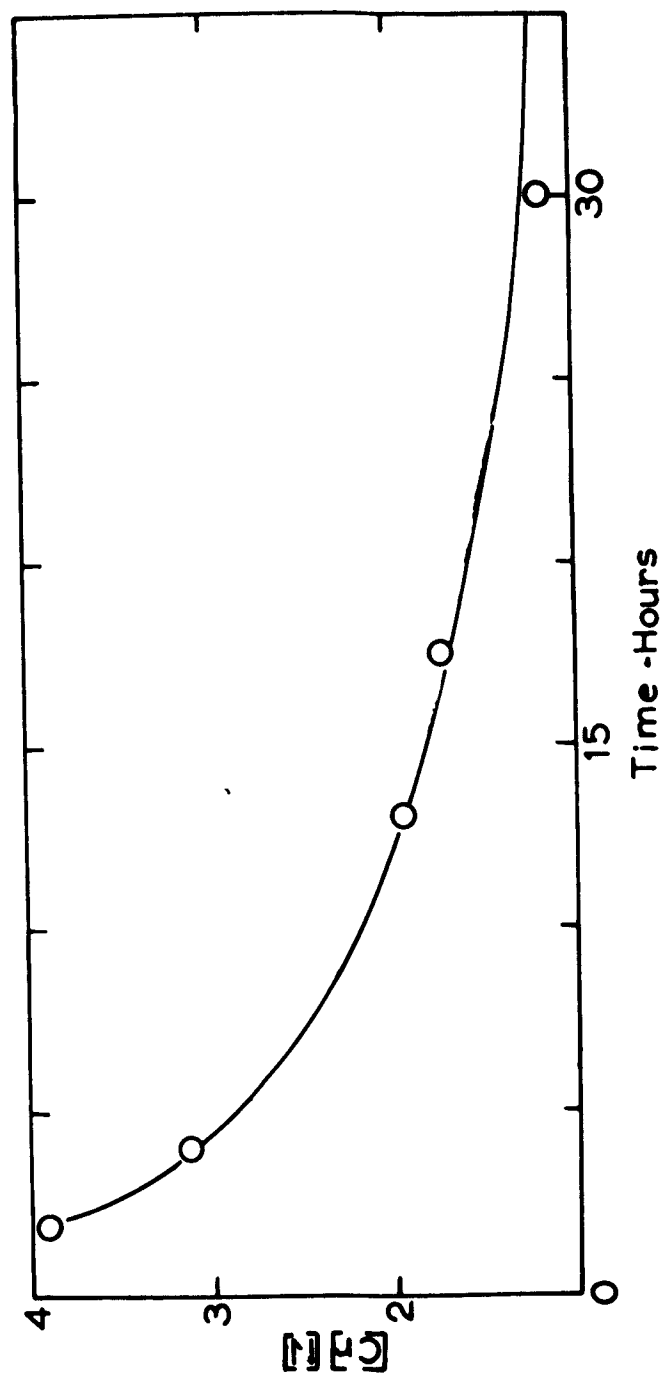


Fig 6 Variation of solubility product with nitriding time.

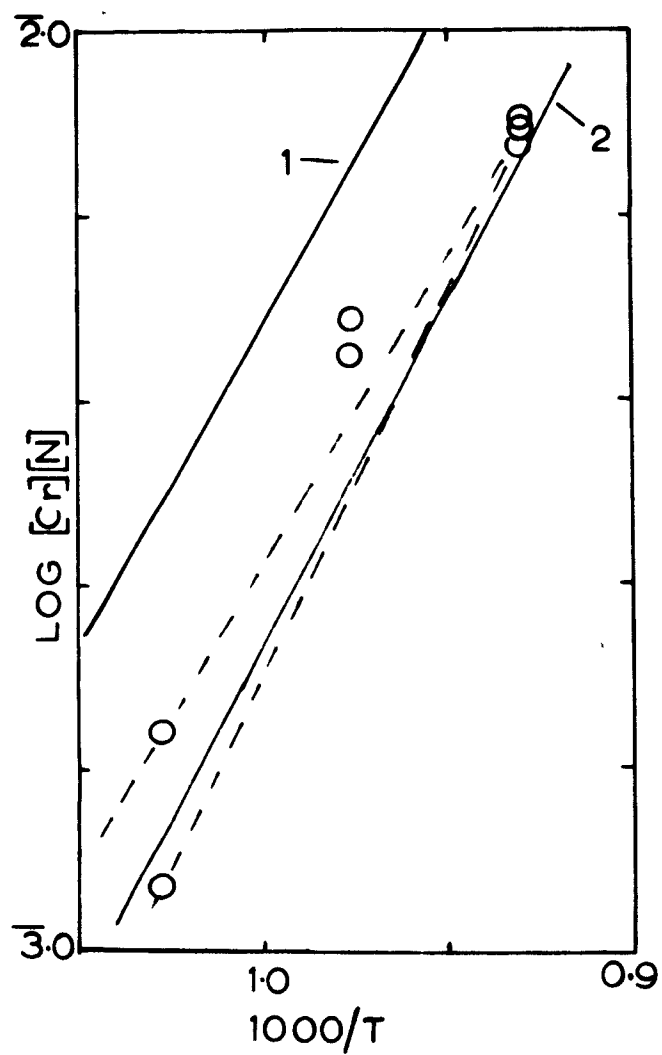


Fig.7 Solubility of CrN in ferrite
 — Calculated. 1 authors } see
 2 Leslie } 1st Report 1961